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LONG-TERM CORROSION POTENTIAL BEHAVIOR OF ALLOY 22 IN HOT
5 *m* CaCl₂ + 5 *m* Ca(NO₃)₂ BRINES

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ABSTRACT

Alloy 22 is a nickel base alloy highly resistant to all forms of corrosion. In very aggressive conditions (e.g. hot concentrated chloride containing brines) Alloy 22 could suffer localized attack, namely pitting and crevice corrosion. The occurrence of localized corrosion in a given environment is governed by the values of the critical potential (E_{crit}) for crevice corrosion and the corrosion potential (E_{corr}) that the alloy may establish in the studied environment. If E_{corr} is equal or higher than E_{crit} , localized corrosion may be expected. This paper discusses the evolution of E_{corr} of Alloy 22 specimens in 5 *m* CaCl₂ + 5 *m* Ca(NO₃)₂ brines at 100°C and 120°C. Two types of specimens were used, polished as-welded (ASW) creviced and non-creviced specimens and as-welded plus solution heat-treated (ASW+SHT) creviced specimens. The latter contained the black annealing oxide film on the surface. Results show that, for all types of Alloy 22 specimens the E_{corr} was higher at 120°C than at 100°C, probably because a more protective film formed at the higher temperature. Specimens with the black oxide film on the surface showed more oscillations in the potential. None of the tested specimens suffered crevice corrosion probably because of the relatively high concentration of nitrate in the electrolyte, $R = [NO_3]/[Cl] = 1$.

Keywords: Alloy 22, N06022, calcium chloride, calcium nitrate, corrosion potential.

INTRODUCTION

Alloy 22 (N06022) is a nickel (Ni) based alloy that contains nominally 22% chromium (Cr), 13% molybdenum (Mo), 3% tungsten (W) and 3% iron (Fe) (ASTM B 575) [1]. Alloy 22 is able to remain passive in most industrial environments because of its high level of Cr, and therefore has an exceptionally low general corrosion rate [2-4]. The presence of Cr, Mo and W in balanced concentrations imparts Alloy 22 with high resistance to localized corrosion such as pitting corrosion, crevice corrosion and stress corrosion cracking even in hot high chloride (Cl⁻) solutions [5-10]. It has been reported that Alloy 22 may suffer crevice corrosion when tightly creviced specimens are anodically polarized in chloride containing solutions [6-8,11-13]. It is also known that the presence of nitrate (NO₃⁻) and other oxyanions in the solution minimizes or eliminates the susceptibility of Alloy 22 to crevice corrosion [6-8,14-23]. An important parameter is the ratio $R = ([NO_3]/[Cl])$ which has a strong effect on the susceptibility of Alloy 22 to crevice corrosion [14-20]. The higher the nitrate to chloride ratio, the stronger the inhibition by nitrate.

From the general and localized corrosion point of view, it is important to know the value of E_{corr} for Alloy 22 under different environmental conditions [16]. The corrosion degradation model for the Yucca Mountain nuclear waste

container assumes that localized corrosion will only occur when E_{corr} is equal or greater than a critical potential (E_{crit}) [16]. This is a necessary but not sufficient condition. That is, in environments that may promote crevice corrosion, if $E_{\text{corr}} < E_{\text{crit}}$ or $\Delta E = E_{\text{crit}} - E_{\text{corr}} > 0$, general or passive corrosion will occur and localized corrosion is not expected. In environments that promote localized corrosion, E_{crit} is the lowest potential that would initiate a localized attack. The value of E_{crit} is generally ascribed as the repassivation potential for crevice corrosion obtained using the cyclic potentiodynamic polarization (CPP) curve described in ASTM G 61 [16]. From the CPP, the repassivation potential may be taken as the potential at which the reverse scan crosses over the forward scan. This potential is called the repassivation potential cross over (ERCO). The repassivation potential could also be taken as ER1 or the potential for which the current density in the reverse scan reaches $1 \mu\text{A}/\text{cm}^2$ [13]. In short, by knowing the values of E_{corr} and E_{crit} (ER1) of Alloy 22, the likelihood or necessary conditions for the alloy to suffer crevice corrosion under natural polarization (e.g. oxygen from air) can be established.

Dunn et al. reported that the values of E_{corr} of Alloy 22 in air saturated 4 M Cl⁻ solution at 95°C were in the range between -300 and -100 mV SCE (-260 to -60 mV SSC) [12]. Similarly, the E_{corr} of Alloy 22 in 0.028 M Cl⁻ pH ~ 10 at 95°C was reported to be between -200 and 0 mV SCE (-160 to +40 mV SSC) [12]. Dunn et al. also stated that low temperature air oxidized specimens produced more scattered values of E_{corr} than did polished specimens [12]. In pH 2.7 solution of 0.028 M NaCl at 95°C the stabilized E_{corr} was approximately +250 mV SCE (+290 mV SSC) [12]. That is, a lower pH promoted a stronger passivation thus resulting in a higher value of E_{corr} . Similar findings were reported by Estill et al. who reported that in acidic multi-ionic solutions simulating concentrated ground water the E_{corr} of Alloy 22 could be as high as +400 mV SSC at 90°C [24]. However, in pH 10 multi-ionic solutions the steady state E_{corr} was below +100 mV SSC [24]. The increase in the value of E_{corr} is generally accompanied by a decrease in the value of corrosion rate [7,25]. For example, it was reported that when Alloy 22 was immersed in aerated simulated acidified water (SAW) at 90°C, the E_{corr} increased from approximately -300 mV to +300 mV SSC in one week [7]. At the same time, the corrosion rate dropped one order of magnitude, from approximately 1 $\mu\text{m}/\text{year}$ after immersion to approximately 0.1 $\mu\text{m}/\text{yr}$ after a one-week exposure [7]. Similarly, creviced Alloy 22 specimens immersed in aerated NaCl + KNO₃ brines at 100°C had corrosion rates in the order of 30 nm/yr after 250 days full immersion [25].

The purpose of the current work was to monitor the behavior of E_{corr} for welded Alloy 22 creviced specimens in 5 M CaCl₂ + 5 M Ca(NO₃)₂ at 100°C and 120°C for more than 720 days. The specimens (creviced and non-creviced) were tested both in the as-welded (ASW) condition and also in the as-welded plus solution heat-treated condition (ASW+SHT). The

latter specimens contained the black annealing oxide film on the surface.

EXPERIMENTAL

The Alloy 22 (N06022) specimens used to assess corrosion potential (E_{corr}) as a function of immersion time were machined from welded 1.25-inch thick plates (~32 mm). Table 1 shows the chemical composition of the heats for the base plate and the welding wire. The plates were welded using the gas tungsten arc welding (GTAW) technique from both sides of the plate using the double V groove technique. The specimens were in the form of prism crevice assemblies (PCA) (Figure 1). The dimensions of the PCA were: 0.375 inch thick, 0.75 inch high and 0.75 inch wide. The exposed surface area of each specimen was 14.06 cm². This surface area did not include the area covered by the crevice formers, which was approximately 1.5 cm². The PCA had a mounting mechanism for the connecting rod explained in ASTM G 5 (Figure 1) [26]. All the specimens had a weld seam through the center of the cross section. The crevice formers were mounted on both sides of the specimen (Figure 1). Each crevice former consisted of a washer made of a ceramic material containing 12 crevicing spots or teeth with gaps in between the teeth (ASTM G 48) [26]. The width of the weld seam was not the same for both faces where the crevice formers (CF) were mounted, that is, in some instances the teeth of the CF were resting solely on weld material and in others on a weld and wrought mix of material. Before mounting them onto the metallic specimens, the CF were covered with thick PTFE military grade tape to ensure a tight crevicing gap. The specimens had a ground surface finish of 600-grit paper. There are two types of PCA specimens in this work: (1) The as-welded (ASW) which were as-received welded specimens and (2) the as-welded plus solution heat treated (ASW + SHT) which were annealed in air for 20 min at 1121°C and then water quenched. The latter specimens were finished with 600-grit paper before the heat treatment but the final oxide formed as a consequence of annealing and water quenching was not disturbed prior to testing. The ASW + SHT specimens were black with slight tones of green, typical of high temperature formed chromium oxide. All the PCA test specimens were fully immersed in the test solution. For each surface and metallurgical condition (ASW and ASW + SHT) there were four PCA specimens of Alloy 22 in each Cell 32 and 33. Each cell also contained two welded 1/4-inch diameter rods of Alloy 22. The rods were machined from welded plates, similarly as the PCA specimens described above. The end of the rods that contained the weld seam was partially immersed in the respective electrolytes. The rods were freshly finished with paper 600. The E_{corr} of all ten Alloy 22 specimens in each cell were monitored continuously.

In each cell, the E_{corr} of a pure platinum rod (ASTM B 561) [1] was also monitored. The platinum rods were 1/8-inch in

diameter and 12-inch long. The Pt rods were immersed 1-inch deep into the electrolyte solutions.

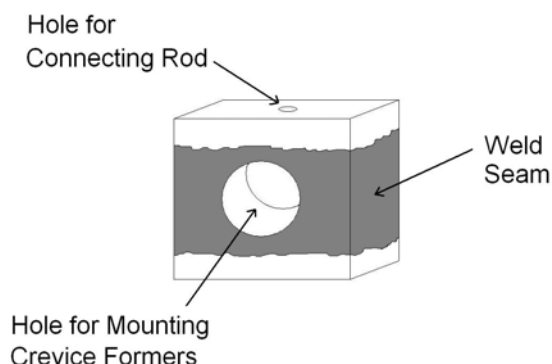


Figure 1. Prism crevice assembly (PCA) specimen

The solutions were prepared using calcium chloride (CaCl_2), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and de-ionized water. The composition of the test solution in both cells was 5 m CaCl_2 + 5 m $\text{Ca}(\text{NO}_3)_2$ where m is the molality (m), which represents moles of the salt per kilogram of the solvent (water). In another concentration units, the electrolyte consisted of 555 g of CaCl_2 plus 820 g of $\text{Ca}(\text{NO}_3)_2$ per 1000 g of water. This represents a concentration of 58 weight percent of salt per mass of solution. The salts were completely soluble at the tested conditions. The measured pH of the solution at ambient temperature was 5.71. The volume of the electrolyte solution in each cell was 2 liters (2 L). The testing temperature was 100°C for Cell 32 and 120°C for Cell 33. The electrolyte solutions were naturally aerated. The solutions were not purged with air, however a stream of air was circulated above the level of the solution. This stream of air exited the vessels (cells) through a condenser to avoid evaporation of the electrolyte.

The E_{corr} was monitored using saturated silver chloride electrodes [SSC] through a Luggin capillary. The reference electrode was kept at room temperature using a jacketed electrode holder through which cooled water was re-circulated. The bridge in the reference electrode was filled with 5 M CaCl_2 solution to keep it liquid at ambient temperatures. The potentials in this paper are reported in the saturated silver chloride scale [SSC or Ag/AgCl]. At ambient temperature, the SSC scale is 199 mV more positive than the normal hydrogen electrode (NHE).

The value of the free corrosion potentials or open circuit potentials were acquired using a commercial data acquisition (DA) unit that had the input resistance set at 10 G-ohm. Typically, the measurements were acquired every minute for the first day and every hour after the first day. The data was logged into in the internal memory of the DA unit and

simultaneously to a spreadsheet in an interfaced personal computer. Usually, data back up was performed monthly.

At the same time that E_{corr} was being monitored for all ten Alloy 22 specimens, the polarization resistance (PR) of three specimens was also monitored as a function of time using the ASTM G 59 technique [26]. Testing of the polarization resistance does not affect the value of the corrosion potential since the polarization is minimal around the value of the rest potential. Polarization resistance measurements were performed in one ASW rod, one ASW PCA and one ASW + SHT PCA specimen in each cell (marked as PR in Table 3). The resistance to polarization was generally measured at 24 h of the first immersion, at 7 days, at 28 days and at every four weeks after that. Values of polarization resistance are not reported here.

Table 1. N06022 Alloy Compositions

Nominal ASTM B 575	50-62 Ni + 20-22.5 Cr + 12.5-14.5 Mo + 2.5-3.5 W + 2-6 Fe + (2.5 Co, 0.5 Mn, 0.35 V max)
Base Metal Heat 2277-0- 3183	55.29 Ni + 21.23 Cr + 13.37 Mo + 2.93 W + 3.65 Fe + 1.7 Co + 0.23 Mn + 0.14 V
Weld Wire Heat XX1829BG	59.31 Ni + 20.44 Cr + 14.16 Mo + 3.07 W + 2.2 Fe + 0.21 Mn + 0.15 Cu

RESULTS

Evolution of the Corrosion Potential (E_{corr})

Tables 2 and 3 lists the final value of E_{corr} of Alloy 22 and platinum specimens in Cells 32 and 33. The final E_{corr} is the average value of measured open circuit potential of the last 30 consecutive immersion days. The corresponding standard deviation is also shown. The exposure time for the specimens at 100°C in Cell 32 was 729 days (Table 2) and for the specimens at 120°C in Cell 33 was 723 days (Table 3). The immersion tests for both cells were terminated on 03-Aug-06.

Figures 2-5 show the evolution of the E_{corr} for Alloy 22 specimens as a function of the immersion time in Cell 32. Figure 2 shows the hourly potential for ASW PCA specimens. There were four specimens tested in parallel and all four specimens showed practically the same behavior. In the first 200 days of immersion the potential raised approximately 400 mV (from -200 mV SSC to +200 mV SSC). Then from 200 days to 729 days, the potential changed very little (less than 50 mV).

Table 2. Specimens Tested in Cell 32
Tests started 04-Aug-04 and ended 03-Aug-06.
Total exposure time = 729 days

Specimen ID	Metallurgical Condition, Specimen Type	Average E_{corr} of the last 30 days, mV SSC	
		E_{corr} value	Standard Deviation
WEA022	Pt Wrought Rod	407	7
KE0256	ASW PCA	263	7
KE0257	ASW PCA	244	8
KE0258	ASW PCA	234	8
KE0259	ASW PCA	215	8
KE0226	ASW SHT PCA	416	49
KE0227	ASW SHT PCA	443	32
KE0228	ASW SHT PCA	470	23
KE0229	ASW SHT PCA	464	9
JE2072	ASW Rod	173	9
JE2073	ASW Rod	190	24

Table 3. Specimens Tested in Cell 33
Tests started 10-Aug-04 and ended 03-Aug-06.
Total exposure time = 723 days

Specimen ID	Metallurgical Condition, Specimen Type	Average E_{corr} of the last 30 days, mV SSC	
		E_{corr} value	Standard Deviation
WEA003	Pt Wrought Rod	377	13
KE0260	ASW PCA	482	8
KE0261	ASW PCA	483	7
KE0262	ASW PCA	483	9
KE0263	ASW PCA	483	9
KE0230	ASW SHT PCA	508	10
KE0231	ASW SHT PCA	479	68
KE0232	ASW SHT PCA	513	9
KE0233	ASW SHT PCA	512	11
JE2074	ASW Rod	447	21
JE2075	ASW Rod	453	20

Table 2 shows the final potential for the ASW PCA specimens in Cell 32. The average value of potential for one specimen was very stable (little noise) since the standard deviation for each one of the four specimens was less than 10 mV (Table 2). The average final E_{corr} for the four specimens was $239 \text{ mV} \pm 20 \text{ mV}$. This is highly reproducible number

considering the variations in E_{corr} that may exist between specimen and specimen.

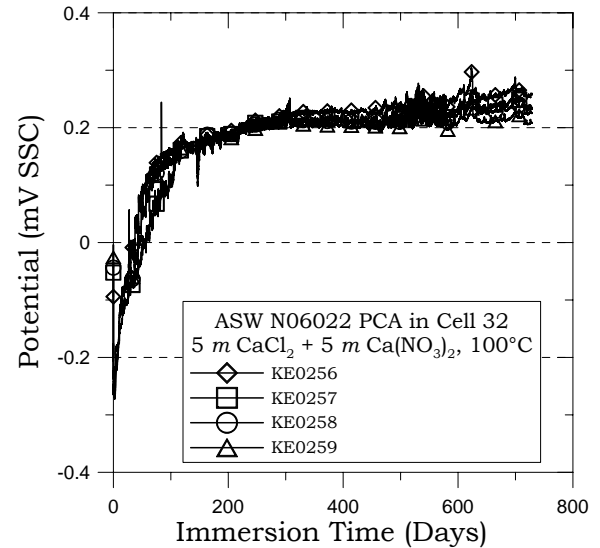


Figure 2. Evolution of E_{corr} for ASW PCA Cell 32

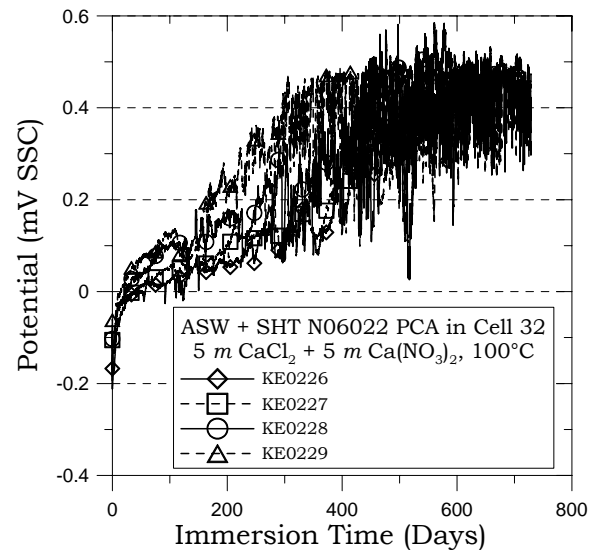


Figure 3. Evolution of E_{corr} for ASW + SHT PCA Cell 32

Figure 3 shows the hourly potential for ASW + SHT PCA specimens. There are four specimens tested in parallel and the four specimens showed similar behavior. However, it is apparent that the amount of noise in the value of potential for the ASW + SHT specimens was larger than for the ASW PCA specimens (Figure 2). The potential for all ASW + SHT PCA seemed to have increased steadily in the first 400 days of immersion and then more or less stabilized. For the entire

exposure time the change in potential was approximately 600 mV (Figure 3).

Table 2 shows the final potential for the ASW + SHT PCA specimens in Cell 32. The average value of potential for one specimen was less steady than for the ASW PCA specimens. There was larger amount of noise and the standard deviation varied from 9 mV to 49 mV. The average final E_{corr} for the four specimens was $448 \text{ mV} \pm 24 \text{ mV}$. This is again a highly reproducible number considering the variations in E_{corr} that may exist between specimen and specimen.

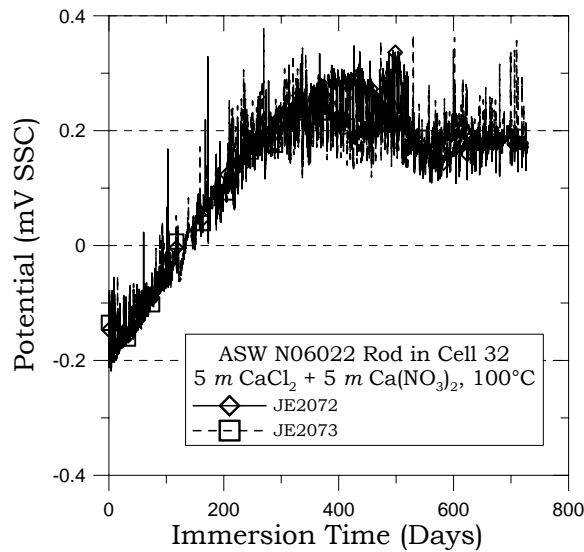


Figure 4. Evolution of E_{corr} for ASW Rod Cell 32

Figure 4 shows the hourly potential for ASW Rod specimens. There are two specimens tested in parallel and both specimens showed similar behavior. However, it is apparent that the amount of noise in the value of potential for the ASW Rod specimens was larger than for the ASW PCA specimens (Figure 2). This could have been a waterline effect since the rod specimens were only partially immersed in the brine. The potential for both ASW rod specimens increased steadily in the first 300 days of immersion and then the potential more or less stabilized at approximately +200 mV SSC. Since immersion, the total change in potential was approximately 400 mV (Figure 4).

Table 2 shows the final potential for the ASW + SHT rods specimens in Cell 32. The average value of potential for each rod specimen was less stable than for each of the ASW PCA specimens but more stable than for ASW + SHT PCA specimens. One rod specimen (JE2073) had larger amount of noise than the other. The average final E_{corr} for both specimens was $182 \text{ mV} \pm 12 \text{ mV SSC}$. This is again a highly reproducible

number considering the variations in E_{corr} that may exist between specimen and specimen.

Figure 5 shows the evolution of the corrosion potential for three types of Alloy 22 specimens (ASW PCA, ASW + SHT PCA and ASW Rod) as well as for platinum (Pt) in Cell 32. Platinum is considered an inert electrode in many environments and therefore the value of E_{corr} of platinum is a measure of the redox potential of the system. The final E_{corr} for the ASW + SHT PCA specimens was even higher than for platinum. The lowest potential corresponded to the rod specimens (Figure 6).

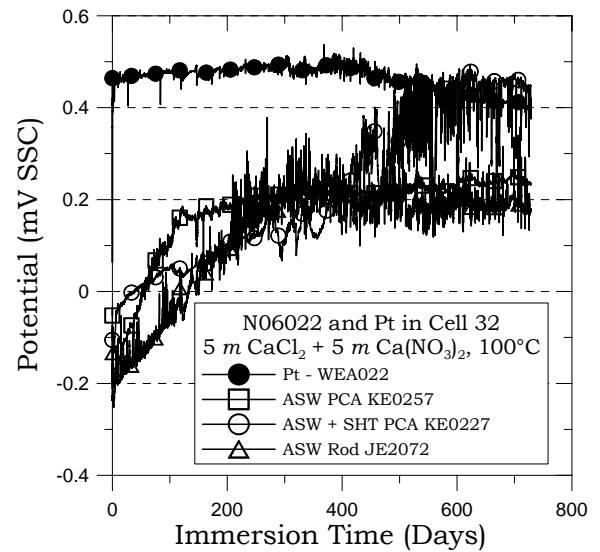


Figure 5. Evolution of E_{corr} for Pt and N06022 Cell 32

Figures 6-9 show the evolution of the E_{corr} for Alloy 22 specimens as a function of the immersion time in Cell 33 at 120°C. Figure 6 shows the hourly potential for ASW PCA specimens. There were four specimens tested in parallel and all four specimens showed practically the same behavior. In the first few days the potential jumped from less than -200 mV SSC to +50 mV SSC. It stabilized at this latter value until day 100. Then the potential started to increase again in the next 300 days and at day 400 it finally stabilized at approximately +480 mV SSC (Table 3). Table 3 shows the final potential for all the ASW PCA specimens in Cell 33. The average value of potential for one specimen was very stable (little noise) since the standard deviation for each one of the four specimens was less than 10 mV (Table 2). The average final E_{corr} for the four specimens was $483 \text{ mV} \pm 1 \text{ mV}$. This reproducibility is extraordinary. That four different specimens would have a corrosion potential differing by only 1 mV after 723 days immersion it is almost implausible.

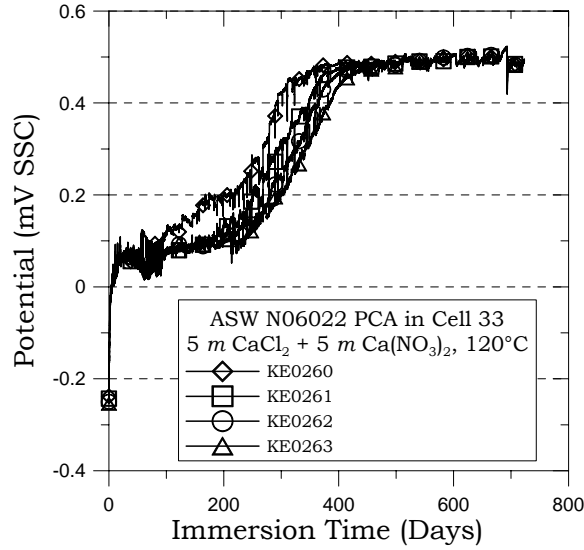


Figure 6. Evolution of E_{corr} for ASW PCA Cell 33

Figure 7 shows the hourly potential for ASW + SHT PCA specimens. There are four specimens tested in parallel and the four specimens showed similar behavior. It is obvious that the potential of these specimens suffered a great deal of noise. Figure 7 shows fluctuations in the order of up to 300 mV. The potential for all ASW + SHT PCA specimens increased rapidly in the first 100 days of immersion and then very slowly for the remainder of the immersion time. For the entire exposure time the change in potential was approximately 600 mV (Figure 3).

Table 3 shows the final potential for the ASW + SHT PCA specimens in Cell 33. The average value of potential for one specimen was less steady than for the ASW PCA specimens (Figure 6). However the standard deviation was not that high considering that the plots in Figure 7 seem noisy. Three specimens had standard deviations between 9 and 11 mV and one specimen (KE0231) had a standard deviation of 68 mV. The average final E_{corr} for the four specimens was $503 \text{ mV} \pm 16 \text{ mV SSC}$. The E_{corr} values are again a highly reproducible.

Figure 8 shows the hourly potential for ASW Rod specimens. There are two specimens tested in parallel and both specimens showed similar behavior at the beginning of the immersion and at the end. There is also noise in the values of potential but the fluctuations are smaller than for the ASW + SHT specimens. Both ASW rod specimens reached their steady state value of potential after approximately 400 days of immersion (Figure 8).

Table 3 shows the final potential for the ASW + SHT rods specimens in Cell 33. The average value of potential for each rod specimen was less stable than for each of the ASW PCA

specimens. The average final E_{corr} for both specimens was $450 \text{ mV} \pm 4 \text{ mV SSC}$. The results are highly reproducible.

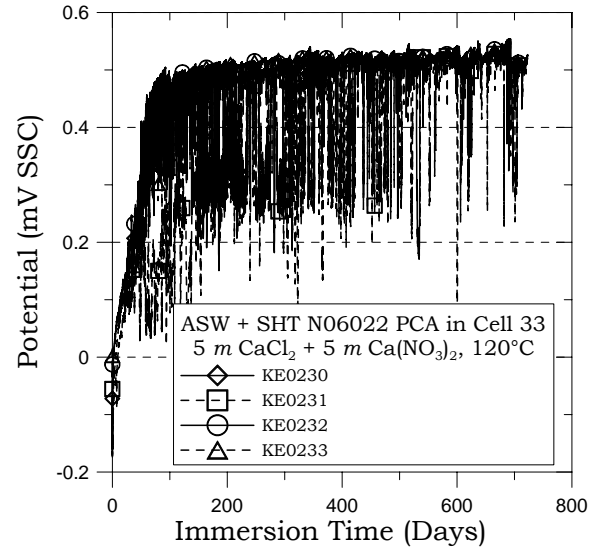


Figure 7. Evolution of E_{corr} for ASW + SHT PCA Cell 33

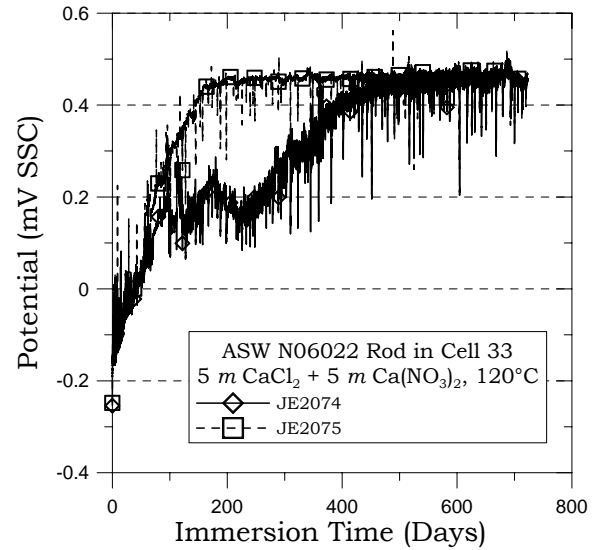


Figure 8. Evolution of E_{corr} for ASW Rod Cell 33

Figure 9 shows the evolution of the corrosion potential for three types of Alloy 22 specimens (ASW PCA, ASW + SHT

PCA and ASW Rod) as well as for platinum (Pt) in Cell 33. The final E_{corr} for all the Alloy 22 specimens was higher than for platinum. The lowest Alloy 22 potential corresponded to the rod specimens and the highest to the ASW + SHT PCA (Figure 9).

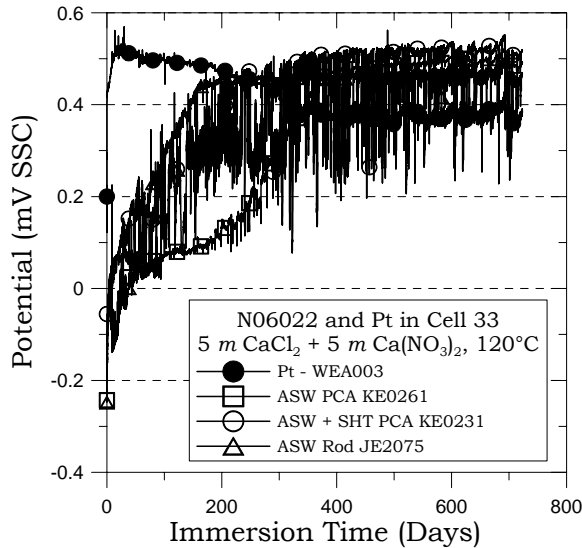


Figure 9. Evolution of E_{corr} for Pt and N06022 Cell 33

Potential Oscillations

Figures 10 and 11 show potential oscillations in more detail. Both figures represent the hourly potential for a period of 2 weeks (14 days) starting in day 600. For this period the potentials of all specimen approximately reached the steady state values (Figures 2-3 and 6-7). In each figure there is the potential for one ASW and one ASW + SHT specimen. Figure 10 shows that while the potential for the ASW PCA specimen had small oscillations, the potential for the ASW + SHT specimen varied by more than 200 mV. Similarly, Figure 11 shows that the potential of the ASW PCA specimen was near noise free while the potential of the ASW + SHT specimen had dips of 200 mV. However, after a couple of days, the potential of the ASW + SHT specimen recovered to the steady state value. Figure 11 also shows that the potential was resting at the steady state value for longer periods and only had occasional dips. That's the reason the standard deviations shown in Tables 2-3 are not as large as one would infer based on the plots in Figures 3 and 7.

It is likely that the oscillations in potential of the ASW + SHT specimens was caused by the presence of the black annealed oxide film on the surface. However the actual effect of the high-temperature air formed film on the potential oscillations is not known. Noisier values of potential for

specimens containing the original oxide scale on the surface have been reported before.

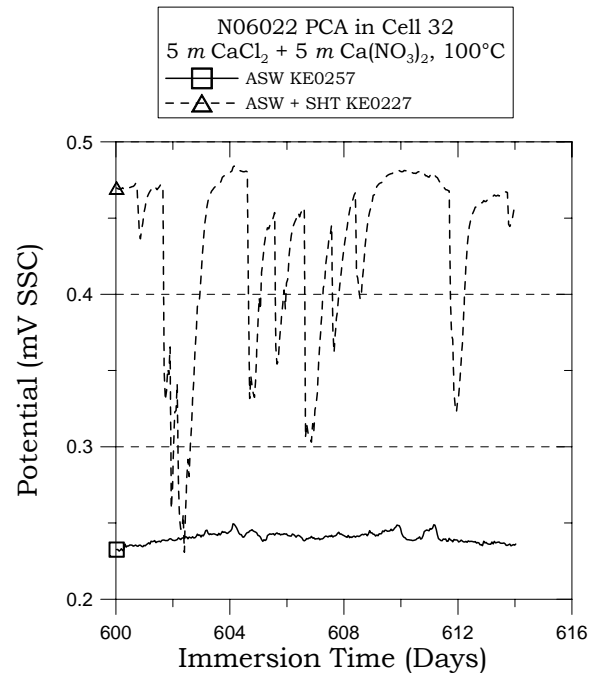


Figure 10. Evolution of E_{corr} for 14 days for ASW and ASW + SHT N06022 in Cell 32

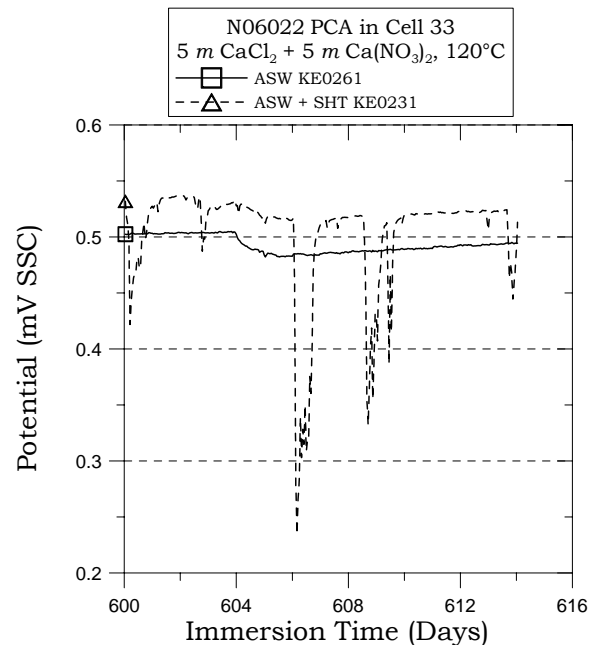


Figure 11. Evolution of E_{corr} for 14 days for ASW and ASW + SHT N06022 in Cell 33

Effect of Temperature on E_{corr}

Table 4 and Figure 12 show that the E_{corr} for the three Alloy 22 specimens was higher at 120°C than at 100°C. Figures 3 and 7 also show that at the higher temperature the specimens reach their steady state value faster than at 100°C. For the three Alloy 22 type specimens the standard deviation at 120°C was smaller than at 100°C, suggesting that the E_{corr} at the higher temperature is more consistent (less error).

Table 4. Average E_{corr} in mV SSC in 5 m CaCl_2 + 5 m $\text{Ca}(\text{NO}_3)_2$

Specimen	Cell 32 – 100°C	Cell 33 – 120°C
Pt	407	377
ASW PCA	239 ± 20	483 ± 1
ASW+ SHT PCA	448 ± 24	503 ± 16
ASW Rod	182 ± 12	450 ± 4

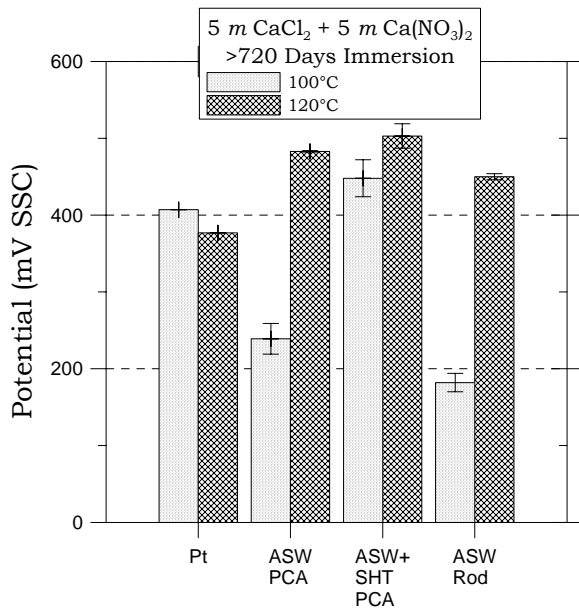


Figure 12. Effect of the temperature on E_{corr}

Table 4 and Figure 12 show that the E_{corr} for platinum was lower at 120°C than at 100°C. This is consistent with what the Nernst equation would predict, that the corrosion potential would decrease as the temperature increased. The opposite behavior of Alloy 22 would suggest that a more protective passive film developed on the surface of Alloy 22 at the higher temperature and therefore the E_{corr} was higher. The passive film

formation on Alloy 22 may have faster kinetics at the higher temperature and therefore the E_{corr} reached steady state values faster than at 100°C.

The fact that the E_{corr} of Alloy 22 at 120°C was higher than the E_{corr} of Pt could be related to the protectiveness of the passive film formed on Alloy 22. The E_{corr} or mixed potential is established by the intersection of the anodic reaction of Alloy 22 with the cathodic reaction in the system. In the present case the cathodic reaction is most likely established by the reduction of oxygen as well as by the reduction of nitrate to lower oxides and even to nitrogen. The more protective the film on Alloy 22 the higher would be the potential at which the reduction reactions intersect the anodic reaction of Alloy 22.

Observation of the Specimens

None of the 20 Alloy 22 specimens exposed to Cells 32 and 33 suffered any type of localized corrosion even after more than 720 days exposure to the hot and highly concentrated brines. None of the creviced specimens suffered any type of crevice corrosion under the crevice formers despite the fact that the crevicing mechanism was very demanding. For each specimen the crevicing mechanism consisted of two rigid ceramic washers covered with PTFE tape. This mechanism provided 24 spots in each specimen where crevice corrosion could have been initiated. The ceramic washer provided the stiffness for the crevice gap and the PTFE tape filled in the voids of the washer. It has been demonstrated before that this crevicing mechanism was the most aggressive ever tested.

After the tests the ASW PCA specimens looked shiny as they were immersed in the solution and the ASW + SHT PCA specimens were black without any type of discoloration. The positions where the crevice formers teeth rested were barely discernible on the surface of the specimens. A few of the ASW PCA specimens exposed to Cell 33 suffered light bluish and golden discoloration on the surface. This may be consequence of the high potentials sustained by the specimens (in the vicinity of +500 mV SSC).

Concluding Remarks

It is known that localized corrosion can occur in Alloy 22 whenever the E_{corr} is equal or greater than the repassivation potential in the tested conditions. That is, if $\Delta E = E_{\text{R1}} - E_{\text{corr}} \geq 0$, localized corrosion will not occur. This is a necessary but not sufficient condition. Current results confirm this rule for localized corrosion prediction. Current results show that even though the corrosion potential of Alloy 22 could be highly anodic (such as in Cell 33), localized corrosion is not going to occur because of other conditions in the system. In Cell 33, even though E_{corr} is near or above 500 mV SSC (Table 4 and Figure 12), the specimens were free from localized corrosion

because the nitrate over chloride ratio was 1, which may have been sufficient in those conditions to inhibit the initiation and propagation of crevice corrosion. It was reported before that even in high temperature brines, when the anionic ratio R is 0.5 and higher, localized corrosion would not occur [27-28].

Current results also confirm that repassivation potentials measured using cyclic potentiodynamic polarization in short term tests in deaerated solutions actually represent the repassivation potential values of Alloy 22 for longer immersion times and under aerated conditions.

SUMMARY AND CONCLUSIONS

Long-term immersion testing have been performed for Alloy 22 specimens in 5 *m* CaCl₂ + 5 *m* Ca(NO₃)₂ solutions at 100°C and 120°C. The specimens were creviced (PCA) and non-creviced (rods)

- The corrosion potential (E_{corr}) for Alloy 22 was higher for the solution heat-treated (SHT) specimens, which contained the air formed black oxide film on the surface.
- The E_{corr} for the SHT specimens fluctuated more than for the freshly polished specimens.
- For each type of specimen, the E_{corr} was higher at 120°C than at 100°C. This suggests that a more protective oxide film formed at the higher temperature.
- The E_{corr} values for each type of specimen were highly reproducible.
- All the specimens immersed in both cells were free from localized corrosion after more than 720 days immersion in the hot concentrated brines.
- In spite of the high reached corrosion potentials, the specimens were free from localized corrosion probably because of the high relative amount of nitrate in the solutions.

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